Applied Quantum Chemistry Calculations

Igor J. Eberstein/587

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Robert H. Goddard

- It is difficult to say what is impossible, for the dream of yesterday is the hope of today and the reality of tomorrow.
- Applied Quantum mechanics fits the above quote superbly well.

Applied Quantum Mechanics

- The dream of yesterday: Use quantum mechanics to understand spectroscopic data.
- The hope of today: Calculate atomic and molecular properties on a sub-microscopic level using the Schroedinger equation
- The reality of tomorrow: Use quantum mechanical calculations to solve practical engineering problems.

Programmatic Usefulness

- Lasers in Space: Problems with mirrors and windows are initiated on the molecular level.
- Infrared Studies of Planetary Atmospheres: Calculation of dipole and multipole moments, transition probabilites, and infrared absorption and emission observed by spacecraft studying Mars, Saturn, Titan, especially on the Cassini mission.

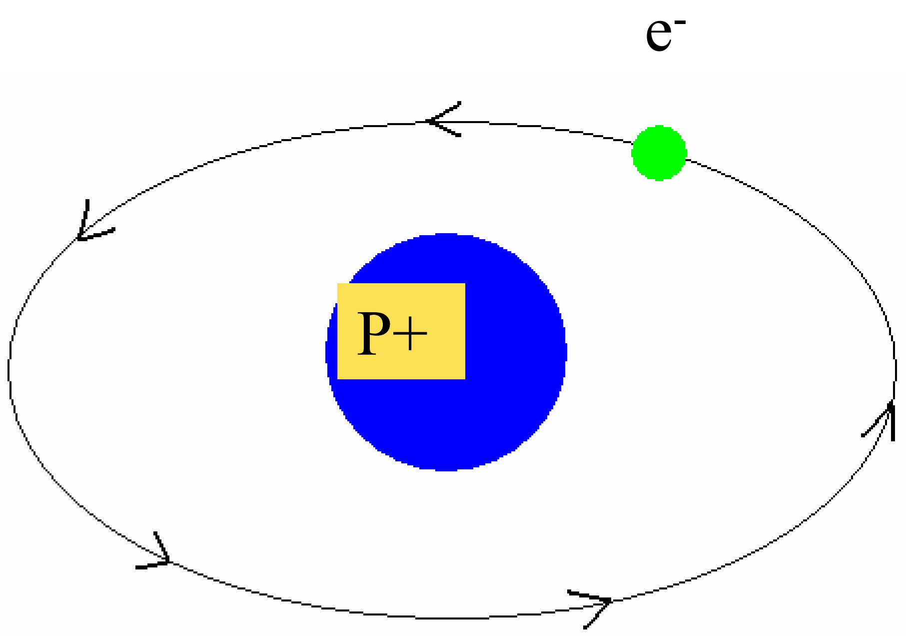
The dream of yesterday

- Spectra occur when light is passed through a prism. Remember VIBGYOR.
- When light passes through a gas before going through a prism, then you get a characteristic spectral signature which looks like a bar code.
- Spectroscopic data were not understood before the advent of quantum mechanics

The Einstein Equation

- The photo-electric effect:
- E=hv
- The energy of electrons emitted from a hot metal surface depends only on the frequency of the light, but not on its intensity.
- Physicists now knew that spectral frequencies were related to energies, but they did not know what the relationship was.

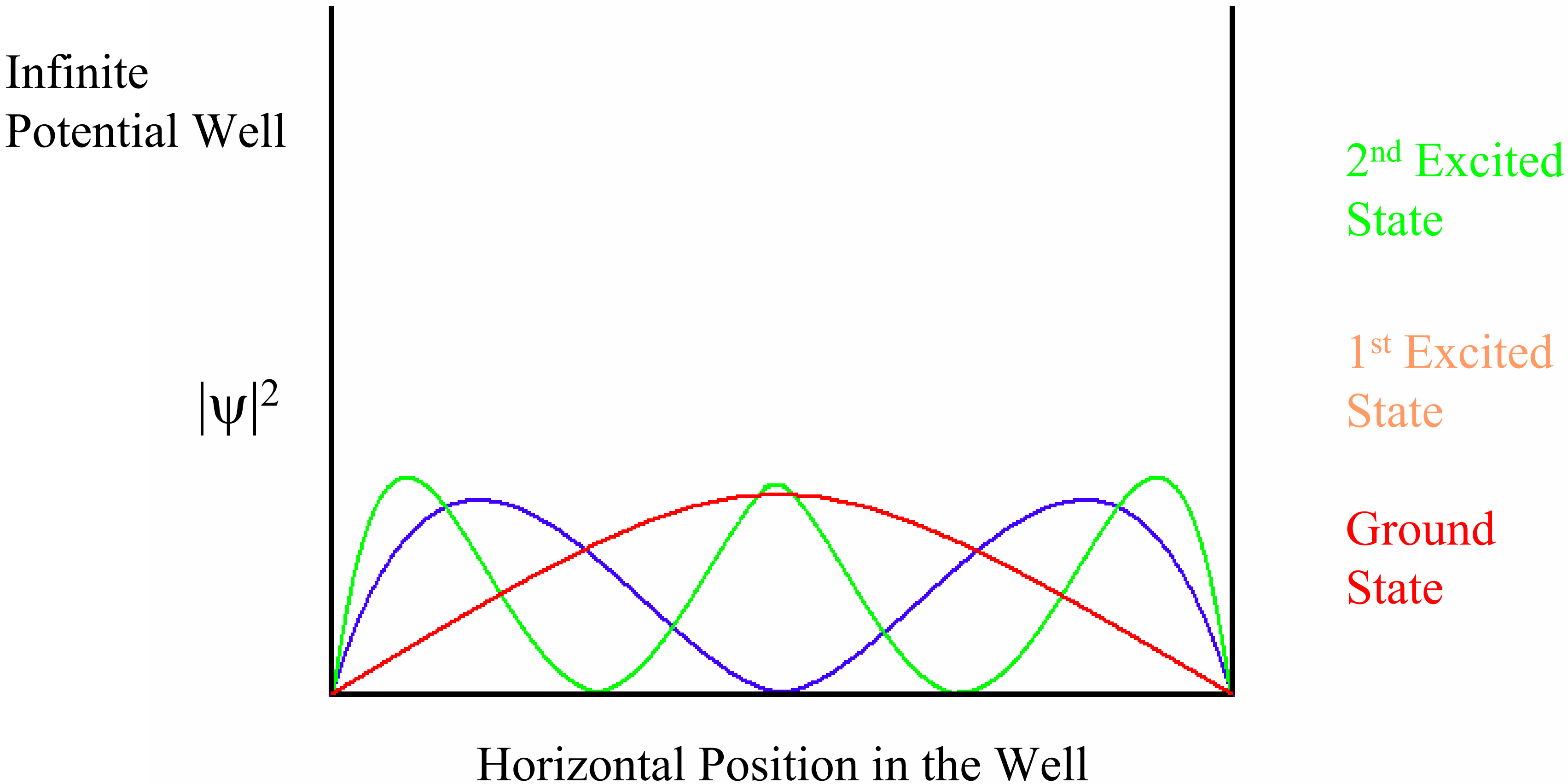
The Bohr Model of the Hydrogen Atom



Niels Bohr lived in Denmark,
the home of the famous astronomer Tyho Brahe

The Time-Independent Schrödinger Wave Equation in One-Dimension

$$[(-h^2/8\pi^2 m)d^2/dx^2 + V(x)]\ \psi(x)=E\ \psi(x)$$



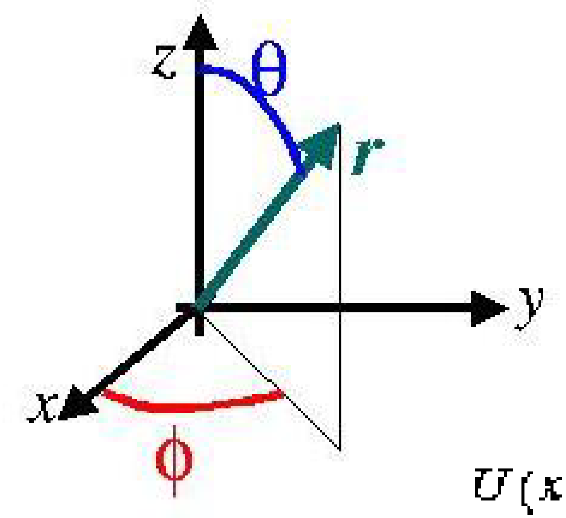
Schroedinger Equation

- The Schroedinger equation is an eigenvalue equation which may be written as:
- HX=E(n)X
- Where H is the Hamiltonian
- E(n); n=1,2,3,… are the eigen-energies which make up the spectral signature.

The Hope of Today

- Calculate atomic and molecular properties on a sub-microscopic level using using the Schroedinger equation

Radial coordinates



$$U(x,y,z) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{\sqrt{x^2+y^2+z^2}} = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r} = U(r)$$

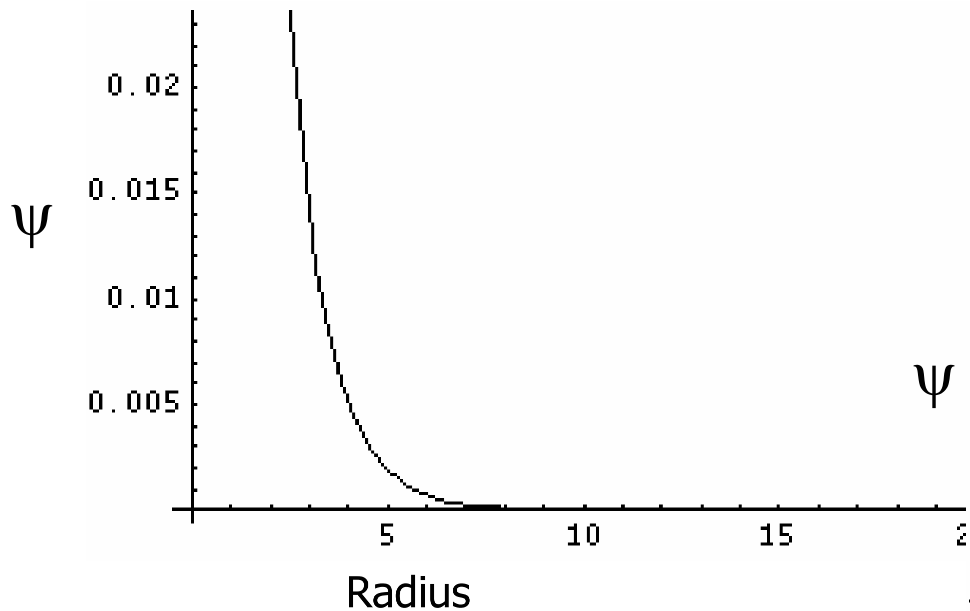
$$-\frac{\hbar^2}{2m}\left[\, \boldsymbol{R''} + \boldsymbol{2/r\, R'} \,\right] + U(r)\,\boldsymbol{R} = E\,\boldsymbol{R(r)}$$

U(r) = a/r, where a is a constant

Solution to the Schrödinger Equation for a Hydrogen Atom

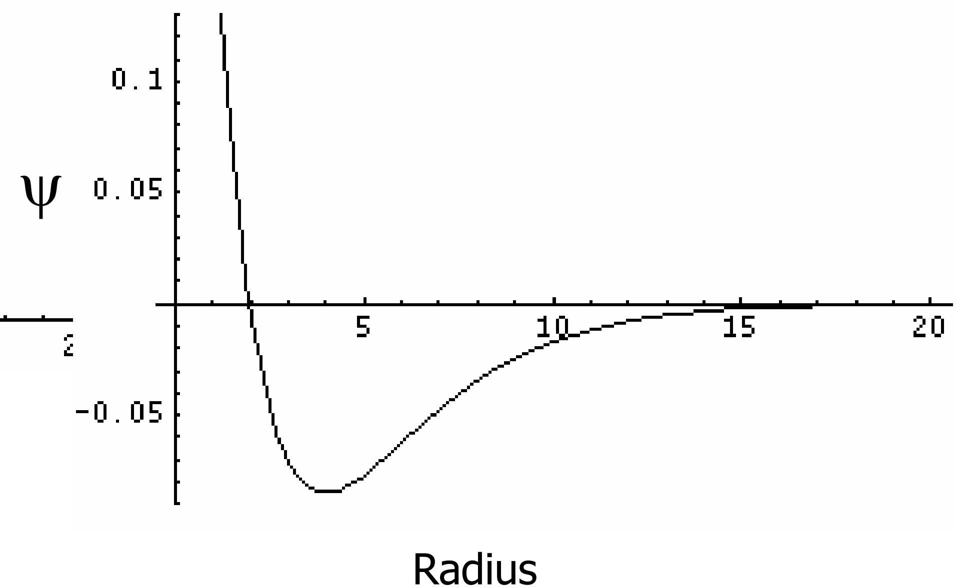
The 1s wavefunction (Ground state)

$$1s = 1/\pi^{1/2} (Z/a)^{3/2} e^{-Zr/a}$$



The 2s wavefunction (1st excited state)

$$2s = 1/4(2\pi)^{1/2} (Z/a)^{3/2} (2\text{-}Zr/a)\, e^{-Zr/2a}$$



Three-Body Problem

- Three-body problem requires numerical solution
- Born-Oppenheimer approximation assumes that electrons instantaneously adjust themselves to the positions of the nuclei.
- Hartree-Fock method represents the simplest numerical solution to a multi-body problem

Fourier Series

- Any function can be approximated by Fourier series (Fourier series is made up of sine waves).

- Fourier series is the simplest basis set.

- More complicated basis sets will be shown later.

Slater Type Orbital (Exponential)

Basis Function = N * $e^{(-alpha * r)}$

where:

N = normalization constant

alpha = orbital exponent

r = radius in angstroms

Gaussian Type Functions

Basis Function = N * $e^{(-alpha * r^2)}$

Calculation Parameters

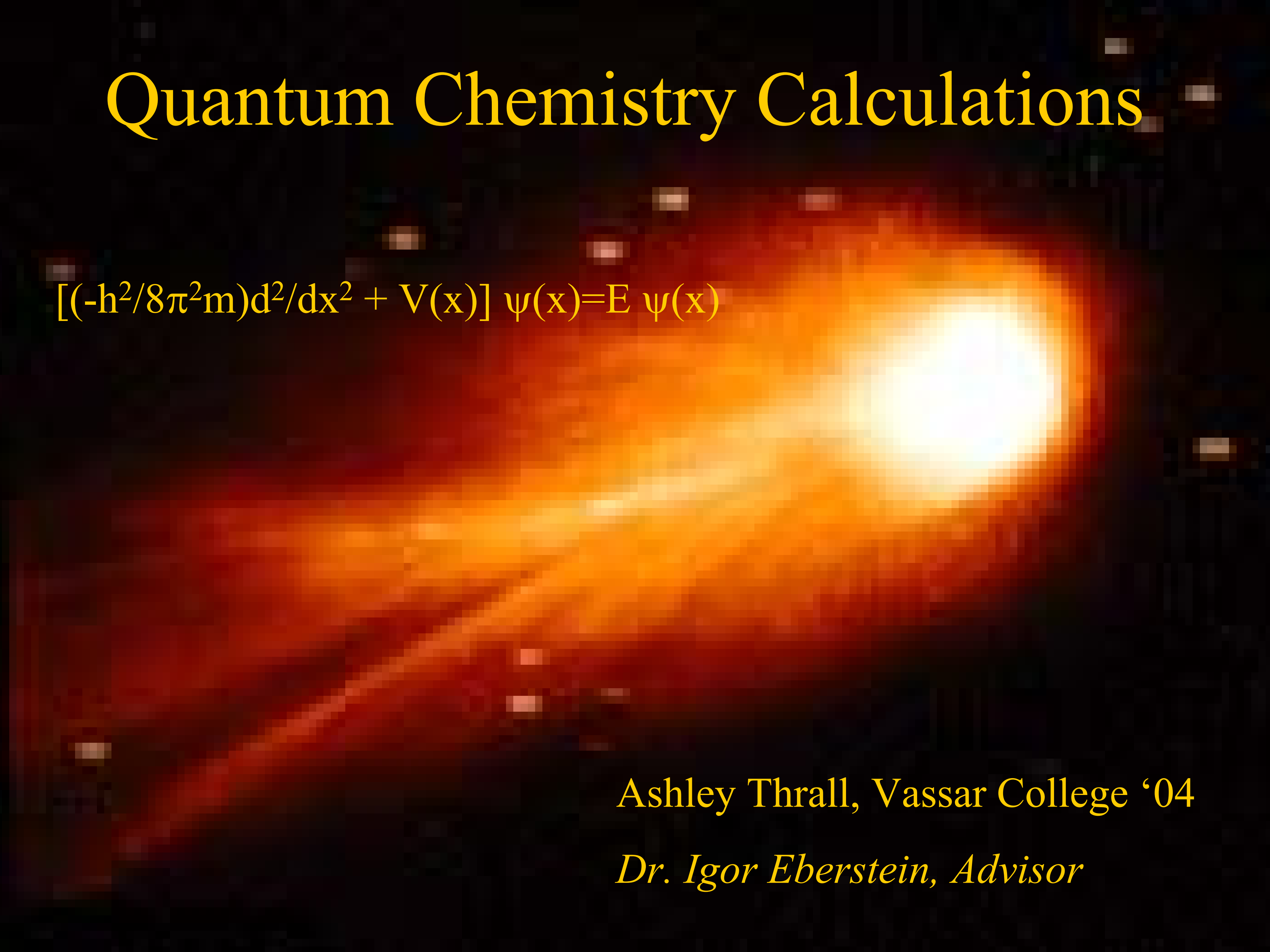
1) **Ab-initio approach** and in particular, **Hartree-Fock method [Self-Consistent Field (SCF)].**

2) **STO** (**Slater Type Orbital**)**-3G basis sets**.

3) For make the calculations easier, STO is approximated by **Gaussian functions**. (ex. **6-31G***)

Quantum Chemistry Calculations

$$[(-h^2/8\pi^2 m)d^2/dx^2 + V(x)]\ \psi(x)=E\ \psi(x)$$



Ashley Thrall, Vassar College ‘04

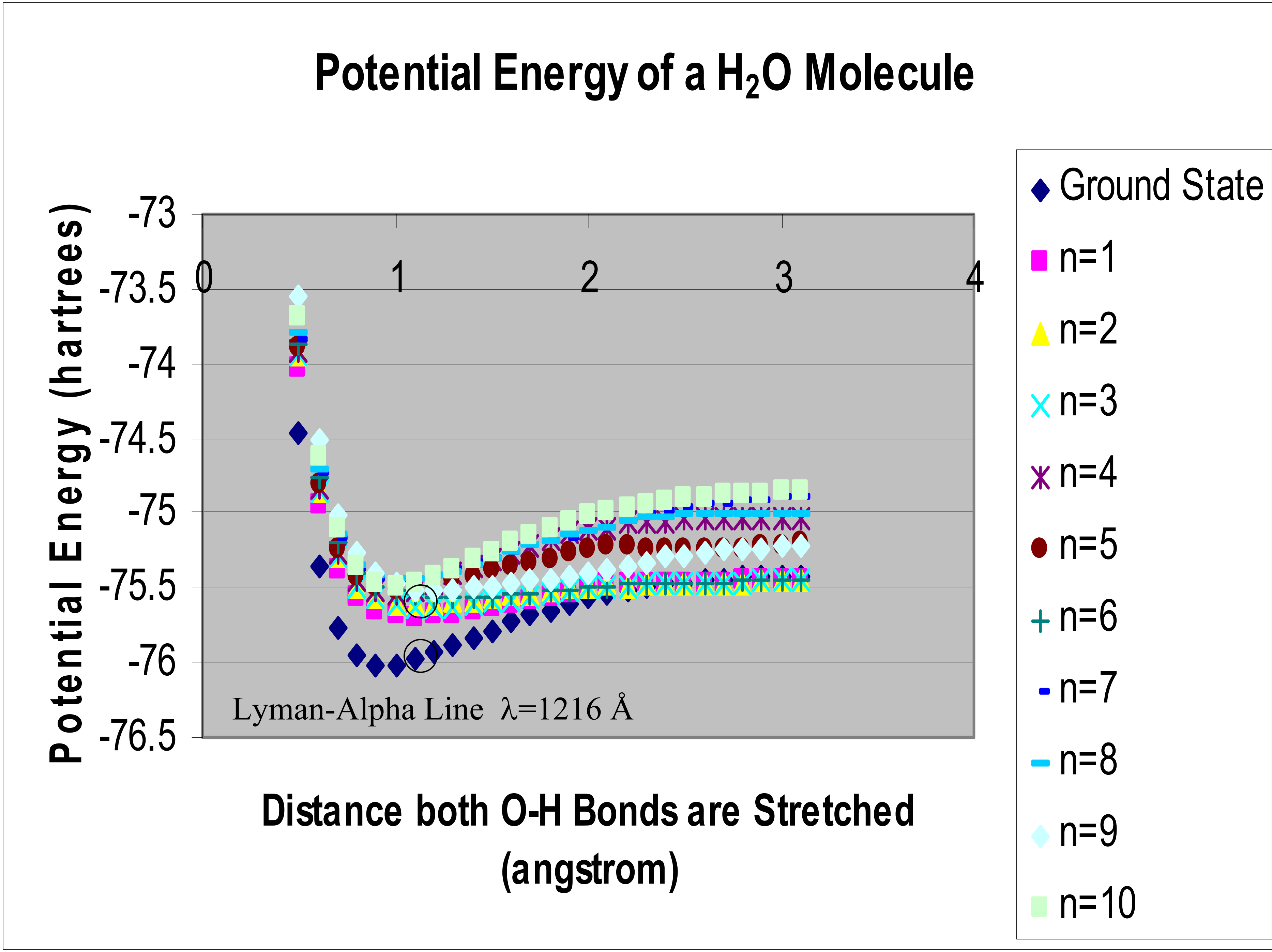
Dr. Igor Eberstein, Advisor

What are Quantum Chemistry Calculations?

It is the calculation of atomic and molecular properties on a sub-microscopic level using the Schrödinger equation.

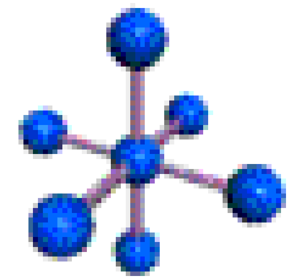
Gaussian98

- Given the molecular structure, Gaussian98 can
  - Calculate the solution to the Schrödinger wave equation (ψ) - the probability distribution of the electrons
  - Use this solution to calculate important qualities of the molecule, such as its energy
- Uses basis sets comprised of Gaussian functions to perform these calculations



Potential Energy of a H_2O Molecule
Potential Energy (hartrees)
-73
-73.5
-74
-74.5
-75
-75.5
-76
-76.5
0
1
2
3
4
Lyman-Alpha Line λ=1216 Å
Distance both O-H Bonds are Stretched (angstrom)
Ground State
n=1
n=2
n=3
n=4
n=5
n=6
n=7
n=8
n=9
n=10

Quantum Chemistry Calculations



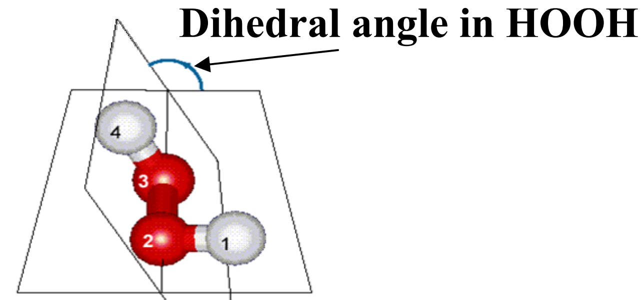
Student Investigator: Juri Yanase
Computer Science Dept.,
Queens College of the City University of New York

Mentor: Dr. Igor Eberstein
NASA Center for Computational Science, Code 931

Three Quantum Chemistry Software Packages:

1) **Gaussian98**
   - Gaussian Inc
   - Ab-initio calculations
2) **GAMESS**
   - Gordon research group at Iowa State University
   - Ab-initio calculations
3) **Dalton**
   - University of Oslo, Norway
   - Ab-initio calculations (Self-Consistent Field (SCF), Møller-Plesset Perturbation Theory (MP2), or Multi-Configuration Self Consistent Field (MCSCF) wave functions)

Z-matrix



Example of hydrogen peroxide H_2O_2

#T HF/STO-3G Opt Test

Atom		Distance to atom			Angle			Dihedral angle		
N1 no.	symbol	N2 no.	N1-N2 Å	special option	N3 no.	N1-N2-N3 degree	special option	N4 no.	N1-N2-N3-N4 degree	special option
1	H									
2	O	1	0.965							
3	O	2	1.464		1	99.6				
4	H	3	0.965		2	99.6		1	111.8	

H_2O Calculations

H2O Calculations		
Reference	**Method/Basis Set**	**Energy(hartree)**
Gaussian98	**HF/STO-3G**	**-74.961**
GAMESS	**RHF, MP2/3-21G**	**-75.585**
Scheiner et al.	SVWN/6-31G**	-75.852
Scheiner et al.	SVWN/UCC	-75.907
Gaussian98	**HF/6-31G***	**-76.012**
DALTON	**SCF/cc-pVDZ**	**-76.026**
Harrison, Handy	CISD/DZ	-76.150
Harrison, Handy	FCI/DZ	-76.158
Frisch et al.	MP2/6-31G**	-76.199
Gauss, Cremer	MP2/6-31G**	-76.205
Frisch et al.	MP2/6-31G**	-76.219
Frisch et al.	MP2/DZP	-76.257
Scuseria, Schaefer	CISD/DZP	-76.258
Experimental Values		-76.480

Levine, Ira N. “Quantum Chemistry” , Prentice Hall, (2000)

Software

Gaussian98:

- Commercial availability and supported.

GAMESS:

- Run in both serial and parallel mode.
- Freely distributed.
- Has graphical capabilities on Macintosh platform.

DALTON:

- Run in both serial and parallel mode.
- Freely distributed.
- Most recent and advanced.

Capabilities

- These packages enable us to determine energy and wavefunction for systems which cannot be solved analytically.

- Because of commercial availability and support, Gaussian98 is user-friendly.

- Since GAMESS and DALTON run in both serial and parallel mode, they are able to handle more CPU intensive calculations. However, they are not user-friendly and not supported.

Computational Costs

- The better approximates, the more computationally difficult and more expensive.

Electron Correlation →

	Basis Set Type	HF	MP2	MP3	MP4	QCISD(T)		Full CI
(ex., STO-3G)	Minimal						...	
(ex., 3-21G)	Split-valence						...	
(ex., 6-31G*)	Polarized						...	
(ex., 6-31+G(d))	Diffuse						...	
	High Ang Moment						...	
	...	...	...	...	...	...	...	
	∞	HF Limit					...	Schroedinger Equation

The Reality of Tomorrow

Engineering Applications of Quantum mechanical software:

Damage to Laser Mirrors.

Infrared Diagnostics of Planetary Atmospheres.

Laser Mirrors

- Substrate for laser mirrors is fused quartz $(SiO_2)_n$
- Adsorbed layer of Silica $(Si(OH)_4)_n$
- Trace amounts of cleaning fluids such as methanol CH_3OH, ethanol C_2H_5OH, benzene, etc.

Radiant Energy Absorption

- Absorption via natural dipole moment
- Absorption via induced dipole moment
- Enhanced absorption via heterodyne effects
- Excessive absorption damages mirror surfaces and degrades laser performance

Status Report on Mirror Damage

- Have begun to develop a strategy to calculate radiative energy damage to laser mirrors.
- Have learned to use some of the software needed for the above calculation strategy.
- This is only the beginning, and much remains to be done.

Infrared Diagnostics of Planetary Atmospheres

- Calculate infrared absorption cross-sections for planetary atmosphere molecules when experimental data is of poor quality or non-existent.
- Work is in a planning stage for Cassini

Summary

- Introduction
- Ashley Thrall work with Gaussian_98
- Juri Yanase work with massively parallel GAMESS and massively parallel DALTON
- Lasers in Space: Problems with mirrors and windows.
- Infrared diagnostics of planetary atmospheres.